(12) UK Patent Application (19) GB (11) 2 299 506 (13) A

(43) Date of A Publication 09.10.1996

(21) Application No 9506839.1

(22) Date of Filing 03.04.1995

(71) Applicant(s)
Unilever Plc

(Incorporated in the United Kingdom)

Unilever House, Blackfriars, LONDON, EC4P 4BQ, United Kingdom

(72) Inventor(s)
Desmond Bernard Hagan
Francis John Leng
Philippa Margaret Smith

(74) Agent and/or Address for Service
P G Mole
Patent Division, Colworth House, Sharnbrook, BEDFORD, MK44 1LQ, United Kingdom

(51) INT CL^6
A61K 7/32

(52) UK CL (Edition O)
A5B BFG B822 B825 B826 B832

(56) Documents Cited
GB 1189216 A EP 0586235 A2 US 3090728 A

(58) Field of Search
UK CL (Edition N) A5B BFG
INT CL^6 A61K 7/32
ON-LINE DATABASES : WPI , CAS ONLINE

(54) Antiperspirant composition comprising titanium

(57) An antiperspirant composition for topical application to the human skin, comprising effective amount of a titanium salt selected from the group consisting of a straight or branched chain saturated or unsaturated non-hydroxy C_2-C_{20} carboxylic acid, C_7-C_{12} aromatic carboxylic acids, ethanolamine complexes, and C_4-C_{12} aliphatic polyols, in a cosmetically suitable vehicle. Examples of compositions include titanium octanoate, titanium oleate, titanium isostearate, titanium decanoate, titanium diethanolamine, titanium triethanolamine and octylene glycol titanate.

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At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

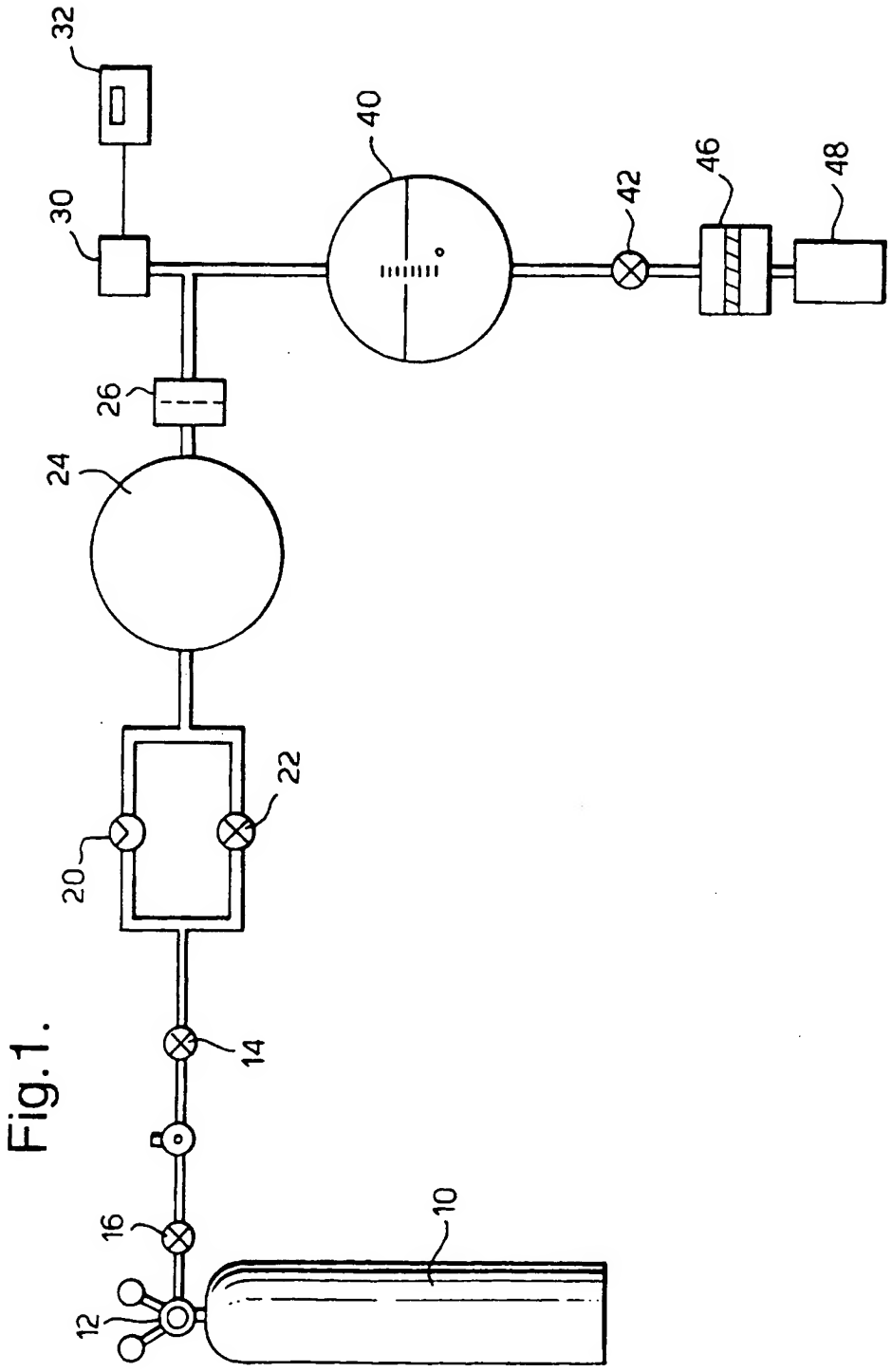

Fig.1.

ANTIPERSPIRANT ACTIVES AND COMPOSITIONS

This invention relates to antiperspirant active materials, and antiperspirant compositions for topical application to the human skin.

The antiperspirant market is dominated by products based on aluminium and/or zirconium salts, which are intended to reduce or prevent perspiration at the skin surface, particularly the underarm.

However, it is known from research into alternative antiperspirant actives that other metal salts may exhibit an antiperspirant effect. One of these metals is titanium.

For example, US 3,090,728 to Carter Products describes the use of certain titanium salts of hydroxy aliphatic carboxylic acids as antiperspirant actives. Salts disclosed in this reference include the mono- and di-acid salts of citrate, gluconate, glycolate, and lactate. However, this reference specifically teaches towards antiperspirant compositions which have a relatively low pH, in the region of pH 2-5. Above this pH, so the reference says, the composition will not be effective. Such compositions with such a low pH are also most likely to cause damage to fabrics and clothing.

EP 586 235 (Unilever) in contrast describes similar compositions to those of the Carter Wallace reference, but in a vehicle having a pH greater than 5, having found that such compositions do indeed have good efficacy.

We have now found that certain other species of titanium salts can be used to produce remarkably good antiperspirant efficacy in topical antiperspirant compositions. These may

have beneficial properties in antiperspirant compositions for topical application over previously utilized titanium salts, including improved efficacy.

Thus, according to the invention, there is provided an antiperspirant composition for topical application to the human skin, comprising effective amount of a titanium salt selected from the group consisting of a straight or branched chain saturated or unsaturated non-hydroxy C_2-C_{20} carboxylic acids, C_7-C_{12} aromatic carboxylic acids, ethanolamine complexes, and C_4-C_{12} aliphatic polyols, in a cosmetically suitable vehicle.

Where the titanium salt is C_2-C_{20} carboxylic acid salt and saturated, it is preferable that the carboxylic acid has a chain length of C_8-C_{12}. Where the titanium salt is C_2-C_{20} carboxylic acid salt and unsaturated or branched chain, it is preferably that the carboxylic acid has a chain length of C_{14}-C_{18}. Preferred titanium nonhydroxy aliphatic carboxylic acids salts for use in compositions according to the invention include titanium octanoate, titanium oleate, titanium isostearate, and titanium decanoate.

Where the titanium salt is a C_7-C_{12} aromatic carboxylic acid, preferably the salt is hydroxylated, as in species such as the titanium salt of salicylic acid (2-hydroxy benzoic acid).

When the titanium salt is an ethanolamine, the titanium salt may conveniently be titanium diethanolamine (e.g. Tyzor DEA, available from Du Pont), or titanium triethanolamine (e.g. Tyzor TE, available from Du Pont, or Tilcom TET, available from Tioxide).

When the titanium salt is a titanium salt of a C_4-C_{12} aliphatic polyol, a preferred species is octylene glycol titanate, available commercially as Tilcom OGT, from Tioxide.

Antiperspirant compositions containing the titanium salts described above have been found to have improved efficacy over other known titanium salts, such as the titanium hydroxy aliphatic carboxylic acid salts described above.

The present invention, and in particular preferred features and embodiments thereof, will now be described in detail.

In the accompanying drawings, Figure 1 is a schematic diagram of the apparatus used to conduct the in vitro test procedure for compositions according to the invention, as described in the Examples below.

Antiperspirant compositions according to the invention can take any convenience product form, including lotion, stick, propellant driven aerosol, cream, and pumpspray formulations.

Preferably, the titanium salt is present in the compositions of the invention at a concentration of from about 0.1 to about 50% by weight of the composition. The amount of the salt required for an effective antiperspirant activity may depend on the product form in which the composition is provided for use.

For example, typical preferred concentrations of the salt in the case of solid sticks, lotions, creams and the like are from about 5 to about 50% by weight of the composition, more preferably from about 5 to about 25% by weight of the composition. In the case of propellant driven aerosol or

pumpspray compositions, for example, the concentration of the salt may typically be lower than the above figures, e.g. preferably in the range of from about 0.1 to about 20% by weight of the total composition, more preferably from about 0.5 to about 15% by weight of the total composition, most preferably from about 1 to about 10% by weight of the total composition.

The pH of the compositions according to the invention may conveniently be adjusted with acids or bases, such as hydrogen chloride or ammonia.

Other Ingredients

The antiperspirant composition according to the invention may comprise other ingredients, depending on the nature and form of the finished product.

Examples of other ingredients which can optionally be present in a composition according to the invention include:

- cosmetically acceptable vehicles, such as straight-chain and branched alcohols, for example ethanol, isopropanol, or isobutanol;
- volatile and non-volatile silicones, such as dimethyl cyclosiloxanes, such as DOW CORNING fluids DC 344 and DC 345, or polydimethylsiloxane, having a viscosity in excess of 5 mm^2s^{-1}, for example from 50 to 100 mm^2s^{-1}, such as DOW CORNING 200 Fluids (standard viscosities 50-1000 mm^2s^{-1});
- deodorants;
- deodorant active perfumes, and deodorant compounds which can also act as antimicrobial agents, such as unsaturated fatty acids, and monoglycerides, for example glycerol monolaurate;
- hydrophobic oils, such as liquid paraffin oils;

- inorganic electrolytes, such as sodium chloride and sodium sulphate
- cationic polymers, such as ABILQUAT 3272 and ABILQUAT 3270, both ex.TH Goldschmidt AG;
- thickeners, such as clays, for example Bentone 38 (trade mark), silicas, for example Aerosol 200 (trade mark), and hydroxypropyl celluloses such Klucel (trade mark);
- skin feel improvers, such as talc and finely divided polyethylene, an example of which is ACUMIST B18;
- gelling agents, such as stearyl alcohol or waxes, for example castor wax;
- emulsifiers, in particular in stick compositions;
- humectants, such as polyols, for example glycerol;
- emollients;
- perfumes;
- preservatives and antioxidants;
- skin benefit agents, such as allantoin;
- colours;
- other cosmetic adjuncts conventionally employed in stick, roll-on lotion, liquid spray, cream, and propellant-driven aerosol antiperspirant products.

The ingredients other than the antiperspirant active can conveniently form the balance of the composition, and accordingly may form up to 99% or more by weight of the total composition, preferably from 50 to 95% by weight of the total composition, most preferably 75-95% by weight of the composition.

Product Form

The composition according to the invention may take the form of liquid or solid product, each of which is suited to, or adapted for, topical application to human skin. One convenient form of the composition according to the

invention is a solid stick, usually contained in a suitable holder or dispenser to enable it to be applied to the area of the skin, particularly the underarm, where control of perspiration and deodorancy is required.

Another form of the composition of the invention is a lotion suitable for inclusion in a roll-on dispenser, fitted with a ball valve, to enable the product to be rolled on to the skin in a manner which is conventional in the art. A further example of a composition according to the invention is the liquid composition for dispensing via a finger-operated pump spray or a hand-operated squeeze spray to provide for delivery to the skin of a finely divided spray or aerosol, without the use of propellant gases to deliver it.

Alternatively, a composition according to the invention can take the form of liquid, containing suspended particulate solids, which is suited to, or adapted for, topical application to human skin from an aerosol container by use of a suitable propellant, examples of which are well known in the art. The aerosol container can then be used to dispense the composition as a spray to enable it to be applied to the area of the skin, particularly the underarm, where control of perspiration and deodorancy is required.

The composition according to the invention can also take the form of a cream, suited to, or adapted for, topical application to the human skin.

Use of the composition

The invention provides for the use of an antiperspirant composition, in accordance with the invention in perspiration control, following topical application to the human skin.

A further preferred aspect of the invention is one which comprises a surfactant which strongly interacts with the skin, thereby causing improved adhesion of the antiperspirant active to the skin. Such surfactants may comprise, for example, cationic surfactants, or alpha-hydroxy acids. Preferably, such additives may be present in the composition at a concentration of from 0.1 to 2% by weight of the total composition.

Examples

The invention will now be further described by way of example only. The following in vitro test procedure was use for evaluation of compositions according to the invention as shown in table 1, uses the apparatus shown in Figure 1. Compositions were made up by diluting the titanium salt in a solvent to the appropriate concentration and testing the solution as described.

In vitro test procedure

Compositions according to the invention were subjected to an **in vitro** test method to investigate their efficacy as antiperspirant actives. The formulation of the compositions used for this test are given in Table 1 below. The % blockage scores quoted are the average of three attempts.

The following describes the apparatus and test protocol used. The apparatus and test protocol are based on the apparatus and method described by H.H. Reller & W.L. Luedders, "Pharmacologic and toxicological effects of topically applied agents on the eccrine sweat glands", Mod. Toxicol. 4: 1-54 (1977).

Apparatus Design

The apparatus used to approximate the degree of pore blocking that would be provided by antiperspirant compositions on the skin surface is shown schematically in figure 1 of the accompanying drawings. The apparatus comprises four major elements, namely:

(a) the pressure control unit,
(b) the sweat reservoir,
(c) the cell and
(d) the detection and measurement system.

(a) Pressure Control Unit (10-32)

A white spot nitrogen cylinder 10 and gas regulator 12 are connected to an on/off isolation valve and pressure release safety valve 16. Stainless tubing and Swagelock couplings are used for subsequent connections. The primary pressure source is followed by a parallel arrangement of needle 20 and on/off 22 valves, a gas ballast reservoir 24 and a 0.5 micron particle filter 26. The unit is terminated via a 0 to 3 Bar pressure transducer 30, with accompanying three and a half digit meter 32.

The pressure unit delivers a controlled pressure, which may be stepped or ramped as a function of time. In these experiments, which were to evaluate flow rates, the stepped mode of the apparatus was used.

The in-line particle filter 26 eliminates contamination of the sweat reservoir 40.

(b) "Sweat" Reservoir (40)

This is a laboratory-grade glass reservoir of one litre capacity. Connection to the preceding pressure unit is via a glass to metal seal and Swagelock coupling. Connection to the subsequent cell 46 is via a rapid action on/of valve 42 and Tygon tubing, terminated in the male portion of a Luer-Lok fitting. The reservoir is easily removed for cleaning. Both the pressure control and reservoir units are enclosed in an aluminium box, for safety reasons. Normal operation involves a maximum pressure of less than one atmosphere above ambient.

(c) Cell (46)

A 5 µm Millipore SM filter was held in a stainless steel Millipore holder with a Luer-Lok fitting. This particular filter has a simple well-defined structure, and is appropriate for the materials tested.

(d) Detection System (48)

Liquid was collected in a measuring cylinder in the flow studies, with the rate of fluid collection being measured.

Experimental

Millipore filters were used for all evaluation of purely aqueous solutions. Where non aqueous solvents were used, the Millipore Fluoropore 5µm filters were used.

The "sweat" reservoir is filled to a predetermined mark with filtered, deionised water and pressurised to 0.2 atmospheres above atmospheric pressure via the pressure unit.

The filter is transferred to the cell, flooded with distilled water and attached to the reservoir, ensuring that all air bubbles have been expelled. A flow experiment is commenced by opening the rapid action valve between the cell and reservoir.

The average of three ten-second collections gives the unblocked filter flow rate. The filter is then impregnated with a test solution of antiperspirant active by immersion for ten minutes.

The filter is removed, gently shaken, and introduced into a "sweat" solution to gel the entrapped test solution. The perspiration perceived as a wetness problem is almost entirely that secreted by the eccrine glands. The fluid released is chiefly water, but the next major component is sodium chloride, typically present at a level of 0.7% by weight. Hence, the immersion for ten minutes in a 0.15M (approximately 0.9% by weight) solution of sodium chloride mimics exposure to sweat.

The average of three further flow experiments gives the blocked filter flow rate.

The in vitro pore blockage is expressed as a Fractional Flow Rate, equivalent to a percentage blocking value, and calculated by:

Fractional Flow Rate (FFR) = (A-B)/A x 100, where A = average unblocked flow rate, and B = average blocked flow rate. Hence B = 0 if there is total blockage, and hence FFR

= 100%. In all cases, the FFR value represents the average of six readings, three for each side of the filter.

EXAMPLE 1

The following additional titanium salts were tested by the test method outlined above, and their degree of in vitro pore blocking determined;

EXAMPLE 1 TABLE 1

Composition (% w/w)

Component	1	2	3	4	5	6	7	8	9	10	11
Titanium decanoate	10	10	-	-	-	-	-	-	-	-	-
Titanium octanoate	-	-	10	10	-	-	-	-	-	-	-
Titanium oleate	-	-	-	-	10	10	-	-	-	-	-
Ethanol	90	-	90	-	-	-	-	-	-	-	90
Isopropyl myristate	-	-	-	-	-	90	-	-	-	-	-
Volatile Silicone	-	90	-	90	90	-	-	-	-	-	-
Butanol	-	-	-	-	-	-	-	90	-	-	-
Isopropyl alcohol	-	-	-	-	-	-	-	-	90	90	-

EXAMPLE 1 TABLE 1 CONT/D

Component	1	2	3	4	5	6	7	8	9	10	11
Water	-	-	-	-	-	-	95	-	-	-	-
Ammonium titanium disalicylate	-	-	-	-	-	-	5	-	-	-	-
Titanium isostearate (Tilcom CA10, ex Tioxide)	-	-	-	-	-	-	-	10	-	-	-
Titanium diethanol-amine (Tyzor DEA, ex Du Pont)	-	-	-	-	-	-	-	-	10	-	-
Titanium triethanol amine (Tyzor TE, ex Du Pont)	-	-	-	-	-	-	-	-	-	10	-
Octylene Glycol titanate (Tilcom OGT, ex Tioxide)	-	-	-	-	-	-	-	-	-	-	10

RESULTS

Formulation	% in vitro pore blocking
1	62
2	50
3	46
4	22
5	29
6	72
7	50
8	27
9	100
10	52
11	36

EXAMPLE 2

The following topical compositions are illustrative of the invention, and may be made be conventional techniques.

Composition 1: Alcoholic Roll-On Antiperspirant

Ingredient	% wt.
Titanium Dioctanoate	15.00
Hydroxypropylcellulose	0.75
Ethanol	65.00
Fragrance	1.00
Distilled Water	to 100.00

Composition 2: Alcoholic Roll-On Antiperspirant

Ingredient	% wt.
Titanium Didecanoate	20.00
Hydroxyethylcellulose	0.60
Ethanol	35.00
Propylene Glycol	2.00
Fragrance	1.00
Distilled Water	to 100.00

Composition 3: Non-Alcoholic Roll-On Antiperspirant

Ingredient	% wt.
Ammonium Titanium Disalicylate	5.00
POE-21 Stearyl Ether	3.00
POE-2 Stearyl Alcohol	1.00
POP-15 Stearyl Alcohol	3.00
Disodium EDTA	0.10
BHT	0.05
Fragrance	1.00
Distilled Water	to 100.00

Composition 4: Roll-On Antiperspirant

Ingredient	% wt.
Titanium Dihexanoate	10.00
Magnesium Aluminium Silicate	1.00
Glycerol Monostearate (acid-stable)	8.00
Cyclomethicone	2.00
Fragrance	1.25
Distilled Water	to 100.00

Composition 5: Dry Roll-On Antiperspirant

Ingredient	% wt.
Diisopropxy Titanium Diisostearate	15.00
Decamethylcyclopentasiloxane	75.00
Dimethicone	5.00
Modified Hydrophobic Clay (Bentone 38)	2.00
Ethanol	3.00
Fragrance	0.50

Composition 6: Aerosol Antiperspirant

Ingredient	% wt.
Titanium Dioleate	16.00
Bentone 38	4.00
PPG-14 Butyl Ether	6.00
Fragrance	4.00
Cyclomethicone	70.00

Base used as 25% by weight of formulation with 75% hydrocarbon propellant.

Composition 7: Aerosol Antiperspirant

Ingredient	% wt.
Diisopropoxy Titanium Dimyristate	45.00
Fumed Silica	8.00
IPM	37.00
Fragrance	10.00

Base used as 23% by weight of formulation with 77% hydrocarbon propellant.

Composition 8: Aerosol Antiperspirant

Ingredient	% wt.
Solid Titanium Diethanolamine	6.00
Bentone 38 (Hydrophobic Clay Derivative)	2.00
Ethanol	9.50
Urea	0.50
Cyclomethicone Pentamer Blend	1.00
Perfume	1.00
Pentane	37.00
Hydrocarbon Propellant (CAP 30)	43.00

Composition 9: Dry Suspensoid Stick Antiperspirant

Ingredient	% wt.
Titanium Triethanolamine	20.00
Stearyl Alcohol	23.00
Hydrogenated Castor Oil	4.00
Glycerol Monostearate	1.00
PPG-14 Butyl Ether	2.00
Magnesium Aluminium Silicate	1.00
Perfume	1.00
Cyclomethicone Pentamer Blend	47.00

Composition 10: Dry Suspensoid Stick Antiperspirant

Ingredient	% wt.
Octyleneglycol Titanate	30.00
Stearyl Alcohol	20.00
Hydrogenated Castor Oil	4.00
BHT	0.05
PEG-150 Distearate	1.00
Magnesium Aluminium Silicate	3.20
Perfume	1.50
Cyclomethicone Pentamer/Tetramer Blend	40.25

Composition 11: Unfragranced Dry Suspensoid Stick Antiperspirant

Ingredient	% wt.
Titanium Docosanoate	20.00
Stearyl Alcohol	19.00
Hydrogenated Castor Oil	4.00
Glycerol Tribehenate	2.00
PEG-8 Distearate	1.00
Talc	4.00
Cyclomethicone Pentamer/Tetramer Blend	47.00

Composition 12: Dry Suspensoid Stick Antiperspirant

Ingredient	% wt.
Titanium Octanoate	18.00
Stearyl Alcohol	22.00
PPG-2 Myristyl Ether Propionate	46.00
Glycerol Tribehenate	2.00
PPG-15 Stearyl Ether	6.00
Silicone Dioxide	1.00
POE-5 Oleyl Ether	1.00
C18-C36 Triglycerides	4.00

Composition 13: Gel Antiperspirant

Ingredient	% wt.
Titanium Diethanolamine (50% solution in isopropyl alcohol)	40.00
Propylene Glycol	10.00
Water	50.00

Composition 14: Stick

Ingredient	% wt.
Octyleneglycol Titanate	10.00
Dibenxylidene Sorbitol	3.00
Ethanol	41.00
Propylene Glycol	30.00
Zinc Acetate	0.50
Stearic Acid	0.50
Cyclomethicone Pentamer Blend	10.00
POP-15 Stearyl Alcohol	5.00

Composition 15: Stick

Ingredient	% wt.
Diisopropyl Titanium Dioleate	13.00
Bentone 38	6.00
Behenyl Alcohol	13.00
Propylene Glycol	20.00
Dipropyleneglycol Methyl Ether	7.00
Talc	4.00
Cyclomethicone Tetramer Blend	4.00
Perfume	1.00
Ethanol	22.00

Composition 16: Unfragranced Pump Antiperspirant

Ingredient	% wt.
Dipotassium Titanium Disalicylate	15.00
Ethanol	72.00
Hydrogenated Castor Oil	1.00
Isopropyl Myristate	6.00
Propylene Glycol	6.00

Composition 17: Pump

Ingredient	% wt.
Titanium Didecanoate	20.00
Ethanol	59.50
Perfume	0.50
POP-15 Stearyl Alcohol	2.00
Stearic Acid	2.00
Cyclomethicone Tetramer/Pentamer Blend	16.00

Composition 18: Pump

Ingredient	% wt.
Diisopropyl Titanium Dioctanoate	10.00
Ethanol	80.00
Perfume	1.00
Stearic Acid	3.00
Propylene Glycol	5.00
Isopropyl Myristate	1.00

CLAIMS

1. An antiperspirant composition for topical application to the human skin, comprising effective amount of a titanium salt selected from the group consisting of a straight or branched chain saturated or unsaturated non-hydroxy C_2-C_{20} carboxylic acid C_7-C_{12} aromatic carboxylic acids, ethanolamine complexes, and C_4-C_{12} aliphatic polyols, in a cosmetically suitable vehicle.

2. An antiperspirant composition according to claim 1, wherein the titanium salt is a C_8-C_{12} saturated non hydroxy carboxylic acid.

3. An antiperspirant composition according to claim 1, wherein the titanium salt is a C_{14}-C_{18} unsaturated or branched chain nonhydroxy carboxylic acid.

4. An antiperspirant composition according to claim 1, wherein the titanium salt is titanium octanoate, titanium oleate titanium isostearate, or titanium decanoate.

5. An antiperspirant composition according to any of the preceding claims, wherein the titanium salt is present in the composition at a level of 0.1-50% by weight of the composition.

Patents Act 1977 Examiner's report to the Comptroller under Section 17 (The Search report) -23-	Application number GB 9506839.1
Relevant Technical Fields (i) UK Cl (Ed.N) A5B (BFG) (ii) Int Cl (Ed.6) A61K 7/32	Search Examiner DR C L DAVIES Date of completion of Search 16 JUNE 1995
Databases (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications. (ii) ONLINE DATABASES: WPI, CAS ONLINE	Documents considered relevant following a search in respect of Claims :- 1-5

Categories of documents

X:	Document indicating lack of novelty or of inventive step.	P:	Document published on or after the declared priority date but before the filing date of the present application.
Y:	Document indicating lack of inventive step if combined with one or more other documents of the same category.	E:	Patent document published on or after, but with priority date earlier than, the filing date of the present application.
A:	Document indicating technological background and/or state of the art.	&:	Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
A	GB 1189216	(COLGATE) see page 2 lines 61-64	
A	EP 0586235 A2	(UNILEVER)	
A	US 3090728	(CARTER)	

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